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54 **Fluorine-and chromophore-containing polymer.**

57 Chromophoric-moiety-containing, polymeric materials, containing at least one fluoroaliphatic radical, which are useful as dyes or colorants for fluorine-containing liquids, as coatings or components of coatings which are colored, light-absorbing, or fluorescing and characteristic properties of fluorocarbon polymers, e.g. chemical inertness and hydrophobicity; and a method of detecting leaks in normally sealed devices, e.g. electronic devices, using a coating which includes the polymeric material, and a bath of a fluorine-containing liquid in which the coating is soluble.

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FLUORINE- AND CHROMOPHORE-CONTAINING POLYMER

This invention relates to fluorine-containing polymers. In another aspect, it relates to the method of preparing such polymers. In a further aspect it relates to a method of dyeing fluorine-containing liquids. In still a further aspect, it relates to a method of making selectively soluble or chemically inert coatings of fluorine-containing polymers. In still a further aspect, it relates to a method of detecting leaks in normally sealed, fluid-containing devices such as electronic devices.

Self-colored, polymeric compounds have been described in the art. In Asquith et al., Self-Coloured Polymers Based on Anthraquinone Residues, Journal of the Society of Dyers and Colourists, April 1977, 114, the author classifies these compounds into categories according to their method of synthesis. The categories include polymers formed by modification of an already synthesized polymer, polymers formed by addition polymerization of dye monomers through olefinic links in which subsequent polymers are generally straight chain or crosslinked structures with chromophore-containing, side-chain groupings, and condensation polymerization usually based on a polyamide or polyester structure in which the chromophore-containing monomer acts as the polyfunctional acid, base, or alcohol. The condensation polymers generally contain the chromophore as an integral part of the main chain.

U.S. Pat. No. 4,619,990 (Elmasry) describes a number of polymeric dyes known in the art and their uses, including dyes with polymeric backbones of polyester, polyurethane, polyamide, and vinyl polymers with pendent phthalocyanine chromophores, and polymeric dyes derived from acrylate or methacrylate monomers with pendent azo, anthraquinone, or triarylmethane dye moieties. Disclosed in Elmasry are thermoplastic, polymeric dyes derived from condensation polymerization or copolymerization of ethylenically unsaturated monomers, with pendent chromophore groups selected from azo, tricyanovinyl, anthraquinone, methine, and indoaniline groups. Various other polymeric dyes are disclosed in the art, see U.K. Pat. No. 1,036,700 (Tadao) homopolymeric pigments containing anthraquinone groups polymerized through ethylenically unsaturated olefinic, e.g. acrylate, linkages, U.S. Pat. No. 3,567,678 (Kalopissis) water soluble polymer with an acrylate or methacrylate backbone, U.S. Pat. No. 3,503,087 (Wolf) water-soluble copolymers consisting of ethylenically unsaturated azo or anthraquinone dye monomers and a water-soluble monomers, U.S. Pat. No. 2,371,002 (Kirby) azo polymeric dyes that are condensation products, where said condensation product is dispersed in a cellulose derivative and treated with a diazonium compound to produce an azo dye in the cellulosic material.

The art also teaches the preparation of non-polymeric dyes with fluorine-containing substituents. U.S. Pat. No. 3,281,426 (Tiers) discloses a process of perfluoroalkylating aromatic compounds whereby one or more perfluoroalkyl chains become attached to an aromatic nucleus. Said process produces compounds which are soluble in some fluorinated solvents forming strongly blue solutions. U.S. Pat. No. 3,933,914 (Coles) discloses non-polymeric, organic dyes having fluoroaliphatic substituents. U.S. Pat. No. 4,585,460 (Schwander) discloses a bis-vinyl or substituted ethyl sulphenyl azo reactive dye. The dye may have substituents on its aromatic nucleus such as fluorine, or a C₁-C₄ alkyl or alkoxy straight chain or branched radical which may be further substituted by halogen, and alkyl or alkoxy straight chain or branched groups which may be further substituted with fluorine. The dye also has a radical of a coupling component, attached through an azo group, which may have substituents as given above. There have also been a number of disclosures of non-polymeric dyes with F or CF₃ substituents, see U.S. Pat. No. 4,544,738 (Baumann), U.S. Pat. No. 4,548,613 (Bode), U.S. Pat. No. 4,560,744 (Baumann), U.S. Pat. No. 4,582,509 (Buhler).

This invention provides a new class of normally solid, fluorine-containing polymers which are inherently colored, light absorbing, or fluorescing and are preferably insoluble, at 20° C, in water and common, non-fluorinated, organic solvents, e.g. toluene and acetone, and generally soluble, at 20° C, in fluorinated liquids, e.g. 1,1,2-trichloro-2,2,1-trifluoroethane sold as "FREON 113" or perfluorochemical liquids or mixtures of such liquids like perfluoroalkanes, e.g. perfluorooctane; perfluorotrialkylamines, e.g. perfluorotributylamine; perfluorodialkylether, e.g. perfluorodibutylether. Many of such liquids are commercially available such as "FLUORINERT" electronic fluids from 3M Company, "FREON E" series from DuPont De Nemours and Co., "FLUTEC PP" series from ISC, Ltd., and "GALDEN" Perfluorinated Fluid from Montedison S.P.A..

One class of the polymers of this invention are colored, light-absorbing, or fluorescing polymers which contain fluorine in the form of fluoroaliphatic radicals and comprise interpolymerized repeating units derived from:

(A) partially- or non-fluorinated, non-chromophoric-moiety-containing monomer(s) and (B) partially- or non-fluorinated chromophoric-moiety-containing co-monomer(s), at least one of monomers (A) and (B) contain-

ing said fluoroaliphatic radicals. Said chromophoric moiety is a group of atoms that absorbs actinic radiation, such as visible light and ultra-violet radiation, and provides a colored, fluorescing or light absorbing molecule. The monomers (A) and (B) can be co-polymerized through chain-growth (i.e. addition) or step-growth (e.g. condensation) reactions, but a preferred class of polymers are made by chain-growth polymerizations. Step-growth monomers contain at least one, but preferably two, polymerizable groups such as hydroxyl, carboxyl, haloformic, isocyanato, and amino groups. Chain-growth monomers must have at least one, and preferably only one, ethylenically-unsaturated, polymerizable group such as acrylic, methacrylic, acrylamido, vinyl or allyl groups.

Another class of polymers of this invention are fluorine-containing, colored, light-absorbing or fluorescing, graft polymers which contain fluorine in the form of fluoroaliphatic radicals and are comprised of (1) a polymeric backbone comprising interpolymerized repeating units derived from partially- or non-fluorinated, non-chromophoric-moiety-containing monomer(s) containing at least one polymerizable group, e.g. vinyl, at least one of which monomer(s) contains a reactive group which can be selected from hydroxyl, carboxyl, haloformic, isocyanato, amino, acrylic, methacrylic, vinyl and allyl groups, and (2) at least one pendent group on the polymer backbone, which is derived from partially- or non-fluorinated, chromophoric-moiety-containing, pendent-group-precursor compounds containing at least one reactive group which can be selected from the same class described for said monomer(s) from which the polymeric backbone is derived. The reactive group(s) on the polymer backbone will react with selected reactive group(s) on the pendent-group-precursor compound(s) to form linkages such as carbamate, ester, amide and carbon-carbon linkages, but the reactive groups on the monomers from which the polymeric backbone is derived and the pendent-group-precursor compound(s) must not react with the polymerizable groups on the monomers from which the backbone is derived that react in the polymerization reaction which forms the backbone.

At least one monomer used in making the chain-growth and step-growth polymers, and at least one pendent group of the graft polymer or monomer making up the polymeric backbone of the graft polymer, contains a fluoroaliphatic radical, but preferably a plurality of fluoroaliphatic groups will be incorporated in the polymer and all or substantially all of the fluorine content of the polymer will reside in the plurality of fluoroaliphatic radicals incorporated into the polymer. The fluoroaliphatic radical is a fluorinated, stable, inert, non-polar, preferably saturated, monovalent moiety which is both oleophobic and hydrophobic. It can be straight chain, branched chain, and if sufficiently large, cyclic, or combinations thereof, such as alkyl-cycloaliphatic radicals. The skeletal chain can include catenary oxygen and/or trivalent nitrogen hetero atoms bonded only to carbon atoms, such hetero atoms providing stable linkages between fluorocarbon portions of the radical and not interfering with the inert character of the radical. The R_1 group can be a CF_3 -group, but preferably it is larger and its terminal portion has at least three fully fluorinated carbon atoms, e.g., $CF_3CF_2CF_2$ -, or $(CF_3)_2CF$ - and the preferred compounds are those in which the R_1 group is fully or substantially completely fluorinated as in the case where R_1 is perfluoroalkyl, C_nF_{2n+1} . While the radical can have a large number of carbon atoms, generally the radical will have between 1 and 20 carbon atoms, and 4 to 10 carbon atoms are preferred. The radicals can contain about 40 to 83 weight percent, but preferably about 50 to 78 weight percent, fluorine.

In the interest of brevity, said monomer(s) (A), and co-monomer(s) (B) are respectively referred to, hereinafter on occasion as "non-dye monomers" and "dye monomers". The amount of dye and non-dye monomer(s) used to make the step-growth and chain-growth polymers, and the amounts of polymeric backbone and pendent groups comprising the graft polymer can vary depending on the intensity of color, light absorption or fluorescing properties desired in the polymer, but generally the non-dye monomer(s) or polymeric backbone is a major component of the polymer. Preferably, in the case of step-growth and chain-growth polymers, such polymers can be prepared by polymerizing 90 to 99.9 percent of non-dye monomer(s) with 10 to 0.1 percent of dye monomer(s) on the basis of total monomer weight. In the case of graft polymers, such polymers can be prepared by reacting 90 to 99.9 percent of polymeric backbone, via its reactive groups, with 10 to 0.1 percent pendent-group-precursor compound(s) on the basis of total backbone and pendent group weight.

Some of the polymers of this invention are useful as colored, light absorbing, or fluorescing additives or colorants to impart color, light absorbing or fluorescing properties to fluorine-containing, normally colorless liquid such as perfluorochemical liquids or mixtures of such liquids. Dissolving the polymer in the liquid imparts color, or changes the light absorbing or fluorescing properties, of said fluorinated liquids, aiding in visually distinguishing one liquid from another. Generally, these polymers will be more soluble in the liquid if all or substantially all of their fluorine content resides in fluoroaliphatic radicals incorporated into the polymer and if the polarity of the polymer is similar to that of the liquids into which it is dissolved. Preferably, the fluorine content of the polymer will be about 40 to 70% based on total polymer weight. The polymers can also aid detection of leaks of fluorinated liquids from normally sealed devices, used for the

purpose of heat transfer. Where used in the detection of leaks in heating and cooling equipment, a solution of the polymer in the fluorine-containing, heat transfer liquid is substituted for normally colorless, heat-transfer liquid, thereby making detection of the leaking liquid easier. The polymers can enhance detection of leaks into normally sealed systems, such as semiconductors, or other hermetically sealed electronic devices, using procedures like those described in MIL-STD-883C, Method 1014.8 or MIL-STD-750A, Method 1071. Where used in the detection of leaks in normally sealed systems, the polymer can be dissolved in one of the fluorochemical liquids specified in MIL-STD-883C, Method 1014.8, "Fluorocarbon Gross Leak Test", or MIL-STD-750A, Method 1071, "Fluorocarbon Gross Leak Test", and the procedure is carried out according to the steps specified. The polymer imparts color to or changes the light absorption or fluorescing properties of the bath described in such procedure, making bubbles escaping from the device into the bath easier to detect.

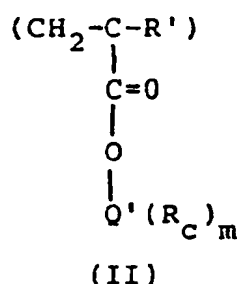
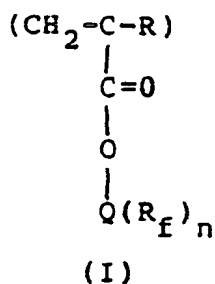
This invention also provides a new method of electronic device leak testing, in which some portion of the surfaces of the internal cavity of a normally sealed device are coated with a film containing at least one of the chromophore-containing polymers and said coating is soluble in a fluorine-containing liquid or mixture of liquids such as those described above. Preferably, the coating is comprised of a film-forming chromophoric-moiety-containing polymer. However, it can be comprised of a mixture of one or more chromophoric-moiety-containing polymer(s) and one or more, non-chromophoric-moiety-containing, film-forming polymers which are compatible; that is, the polymer must remain intimately mixed with the other polymer(s) comprising the mixture without macrophase separation when the mixture is in the solid state. The compatibility of a mixture of polymers is generally determined by trial and error, however, polar polymers, i.e. those containing a plurality of polar moieties such as oxygen atoms, will be more compatible with other polar polymers, e.g. polyester. Non-polar polymers, e.g. those which are predominantly hydrocarbon, will generally be more compatible with other non-polar polymers, e.g. vinyl polymers. Where the coating is comprised of a mixture of polymers, the amounts of each polymer in the mixture can vary widely depending upon the color-imparting or tinctorial strength of the chromophoric-moiety-containing polymer(s), the color, light absorption or fluorescing properties of the coating required, and any effect the chromophoric-moiety-containing polymer(s) may have on reducing the film forming properties of the mixture. In general, the major component of the mixture would be comprised of non-chromophoric-moiety-containing polymer(s), and preferably, chromophoric-moiety-containing polymer(s) can be present at levels of about 0.1-20% based on total mixture weight. The coating can be applied to the surfaces of the normally sealed device from solvent solution by known methods such as spraying, brushing, wire coating, knife coating, curtain coating or gravure coating. The device can then be immersed in a colorless liquid bath comprised of fluorine-containing liquid or a mixture of such liquids, the bath and device may be subjected to the pressurization step described in the fluorocarbon gross leak tests cited above, and the bath is monitored for a change in color, light absorption properties or fluorescing properties caused by the coating dissolving in the liquid that has leaked into the devices' internal cavity, and the subsequent migration of the dissolved, chromophoric-moiety-containing polymer from the internal cavity back into the bath. A change in the bath color, light absorption or fluorescing properties indicates a defective device.

Some of the polymers of this invention are also useful as colored, light absorbing or fluorescing coatings or components of such coatings, that provide the characteristic properties of fluoropolymer coatings, e.g. chemical inertness, electrical non-conductivity, hydrophobicity, oleophobicity, and repellency to silicone oils. Preferably, the coatings are comprised of a film-forming, chromophoric-moiety-containing polymer, however, the coatings may be comprised of a mixture of one or more chromophoric-moiety-containing polymer(s) and one or more compatible, film-forming, non-chromophoric-moiety-containing polymer(s). Where the coating is comprised of a mixture of polymers, the amounts of each polymer in the mixture can vary widely depending upon the desired coating color, fluorescing or light absorption properties, the film-forming properties of the mixture of polymers comprising the coating, and other desired coating physical properties, e.g. chemical inertness. In general, the major component of the mixture is comprised of non-chromophoric-moiety-containing polymer(s). Preferably, the chromophoric-moiety-containing polymer or polymers can be present at levels of about 0.1-20% based on total mixture weight, and the fluorine content of the coating should be at least about 30%. Some examples of such coatings are UV-absorbing, protective coatings for billboards, oil repellent, fluorescing, antimigration coatings for the inside of oil-filled devices, e.g. rocket gyroscopes, to prevent oil leakage from the device and allow visual inspection of the coated surface to ensure it is covered with the coating, electrically non-conducting, chemically inert, protective, copolymer coatings for electronic devices like circuit boards, release coatings, and selectively soluble coatings used as selectively soluble photo resists for imaging systems and electronic chip etching.

The invention permits the adjustment of color, color intensity, and light absorbing or fluorescing

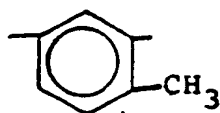
properties of the polymer by controlling the selection and amount of the polymerizable dye monomer(s), or pendent-group-precursor compound(s) incorporated in the polymer. The use of the polymers of this invention as a photo resist in the production of electronic chips offers advantages over currently used photo resists, for example, the non-wetting character of coatings made from the polymers may provide sharper, clearer painted patterns on the chip substrate, and the solvents used to wash the coating off the chip substrate are generally less toxic and less flammable than currently used solvents.

Some of the polymers of this invention can be made by step-growth or chain-growth polymerization reactions, others by graft polymerization, but a preferred class of polymers are made by chain-growth reactions. Step-growth polymers can be derived from mono- or di-functional, or mixtures of mono- and di-functional, non-dye monomer(s), and mono- or di-functional, or mixtures of mono- and di-functional, dye monomer(s). Mono- and di-functional monomers have, respectively, one or two polymerizable groups, that can be selected from hydroxyl, carboxyl, haloformic, isocyanato, or amino groups. Preferably, dye and non-dye monomer(s) are difunctional and the polymerizable groups on all dye monomer(s) are capable of polymerizing through step-growth polymerization reactions with the polymerizable groups on all non-dye monomers. Examples of step-growth polymers are polymers derived from non-dye monomer(s) selected from diacid, dihaloformate, diisocyanate, and diacid halide non-dye monomers, and dye monomer(s) selected from diol and diamino monomers. An example of a graft polymer is one in which the polymeric backbone is derived from monomers with polymerizable acrylic groups, and at least one of the monomers incorporated in the backbone has a reactive group, e.g. hydroxyl, which will not participate in the polymerization reaction, but will react with the reactive group on the pendent-group-precursor compound, e.g. isocyanato. The pendent-group-precursor compound must not contain any group, including its reactive group, that will react with the polymerizable groups on the monomer(s) comprising the polymeric backbone. Chain-growth polymers may be derived from dye and non-dye monomer(s) with ethylenically unsaturated, polymerizable groups, such as acrylic, methacrylic, acrylamido, vinyl, or allyl. Said groups on dye and non-dye monomer(s) need not be identical, and said monomer(s) can have one or more ethylenically unsaturated polymerizable group(s) which need not be identical. However preferably, each monomer will have only one polymerizable group. Some chain-growth polymers will be comprised of interpolymerized units having the general formulas I and II given below:

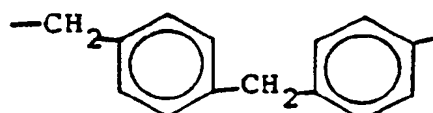


Wherein R and R' are H or CH₃, and Q and Q' are linking groups. Q' can be a valence bond, for example, where a carbon atom of the chromophoric-moiety is bonded or linked directly to the oxygen moiety. Q can also be a valence bond as long as the fluoroaliphatic radical is bonded to the oxygen moiety through a -CHR'' group where R'' is H or alkyl. Q and Q' each can also comprise one or more linking groups such as polyvalent aliphatic moieties, e.g. -CH₂CH₂- and -CH₂CH(CH₂-)₂, polyvalent aromatic moieties,

e.g.



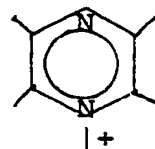
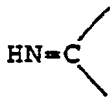
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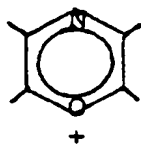
oxy, thio, carboxyl, sulfone, sulfoxo, phosphoxy, -P(O)OH-, amine, e.g. -NH- and -N(C₂H₅)-, or combinations thereof, such as oxyalkylene, iminoalkylene, iminoarylene, sulfonamido, carbonamido, sulfonamido alkylene, carbonamido alkylene, carbamato. R_f is a fluoroaliphatic group, n is a number equal to zero or 1. All type I units incorporated in the polymer need not have the same R, R'' or R_f groups. R_c is an organic radical containing a chromophoric moiety and m is a number greater than or equal to 1. All type II units in the polymer need not have the same R_c or R' groups, but preferably, all R_c groups will be the same and m will

be equal to 1. Type I and II units may be randomly distributed in the polymer. A preferred class of polymers derived from monomers yielding interpolymerized units having general formulas (I) and (II) can be prepared by the chain-growth polymerization of highly fluorinated acrylates and non- or partially-fluorinated, dye acrylates or acrylamides, and optionally, small amounts of other non-dye monomers, such as alkyl acrylates, acrylic acid, vinyl chloride, vinylidene chloride and the like. The molar ratio of dye to non-dye monomer(s) can depend on the intensity of light absorption desired in the final polymer, and on the solubility of the monomers in the reaction solvents (e.g. "FREON 113", 2,3,3-trichloroheptafluorobutane, or combinations of these solvents with non-fluorinated solvents such as ethyl acetate).

Dye monomers and pendent groups used in the invention can be inherently light-absorbing, colored, fluorescent or UV-absorbing and may be partially- or non-fluorinated. Said monomers and pendent groups must have one or more chromophoric moieties of the same or different type, but preferably, only one chromophoric moiety is contained in each monomer or pendent group. Said chromophoric moieties can be selected from the following types as described in D. W. Bannister, A. D. Olin, H. A. Stingl, "Dyes and Dye Intermediates", Kirk-Othmer Encyclopedia of Chemical Technology 3rd Ed., 18, 159-212 (1979):

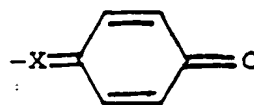
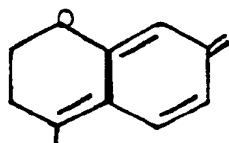


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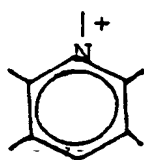
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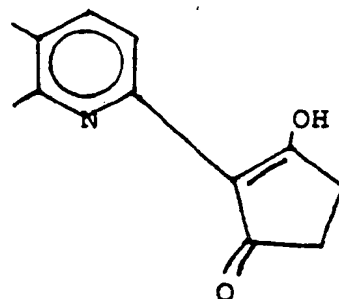
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where X is O or N,

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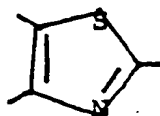


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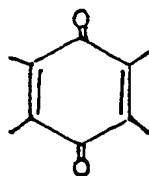
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where X is O or N, moieties with C = N-OH ortho to C = O,

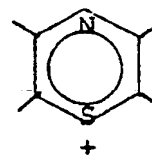
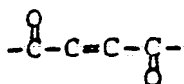
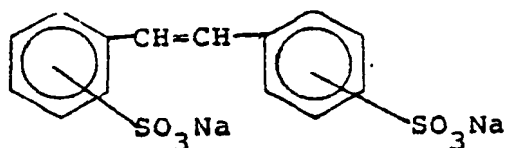
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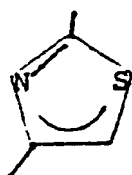
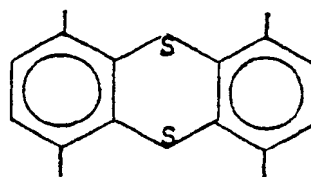
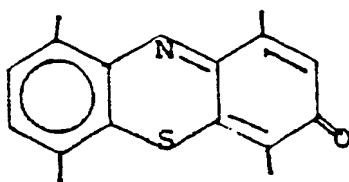
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moieties containing an aromatic ring with a nitro group ortho or para to an amino, hydroxyl or ether group,

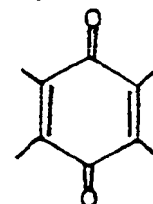
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moieties containing a tetrabenzoporphyrazine group, moieties with a $\text{C}=\text{C}-\text{OH}$ group and a $\text{C}=\text{C}=\text{O}$ group.



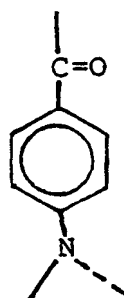
and moieties with both



group

and

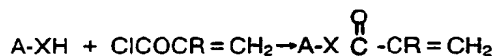
group.



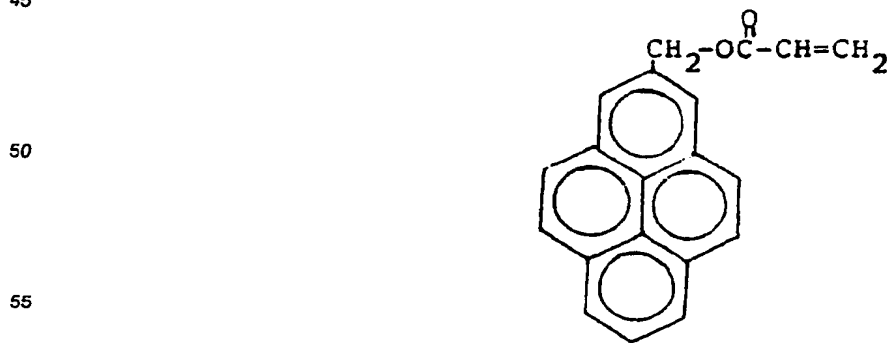
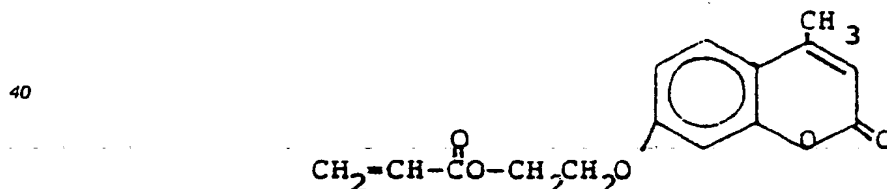
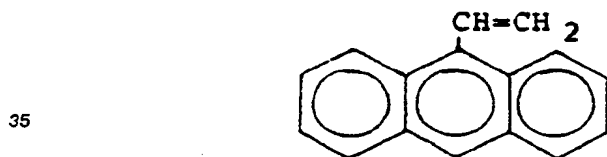
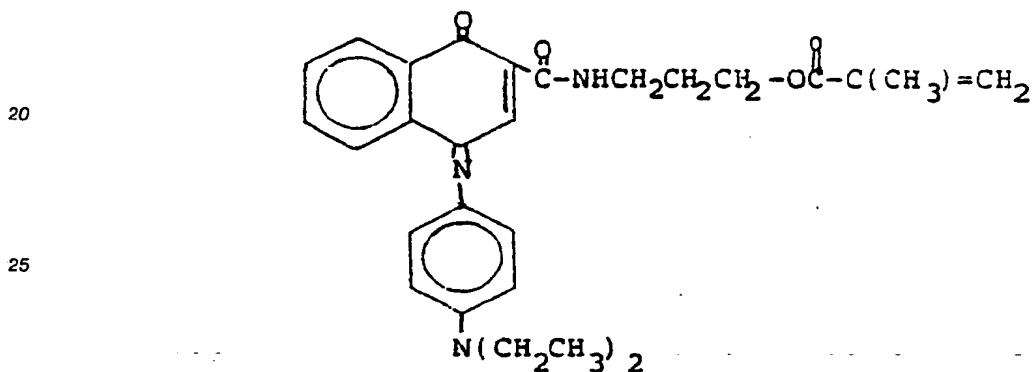
The selection of chromophoric moiety or moieties can determine the color or light absorbing or fluorescing properties of the polymer. The dye monomer(s) for step-growth polymers may be mono- or difunctional, with polymerizable groups that will react with polymerizable groups on at least one of the non-dye monomer(s) or other dye monomer(s), where mixtures of dye monomers are used to derive the polymer, to form linkages through step-growth polymerization reactions. Preferably, said dye monomer(s) will be difunctional and said polymerizable groups will be identical, e.g. dihydroxyl or dicarboxyl. The dye monomer(s) for chain-growth polymers must have at least one ethylenically unsaturated, polymerizable group, and only one such group is preferred, but they may have more than one ethylenically unsaturated group and said groups need not be identical. Said groups can polymerize with ethylenically unsaturated groups on non-dye monomer(s) or dye monomer(s) to form linkages between said monomers through

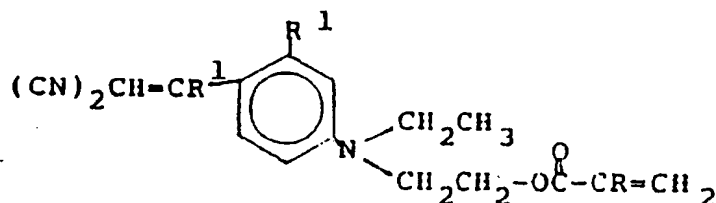
chain-growth polymerization reactions. Preferably, all polymerizable groups on dye monomer(s) will be terminal groups. The pendent-group-precursor compound used to prepare graft polymers will have at least one reactive group chosen, for example, from hydroxyl, carboxyl, haloformic, isocyanato, amino, acrylic, methacrylic, acrylamido, vinyl, or allyl, and this group will not react with polymerizable groups on the non-
 5 dye monomers making up the polymeric backbone.

Commercially available dyes like Disperse Red 17 (color index No. 11210), a diol, available from Crompton and Knowles Corporation, can be used as a dye monomer in step-growth polymerization reactions. A preferred class of dye monomers used in chain-growth polymerization reactions can be prepared from dyes containing hydroxy or amino groups, by reaction with acrylic or methacrylic acid
 10 chlorides via the reaction

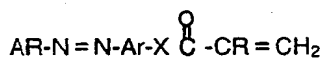


Where A a chromophore-containing group, such as $Ar-N=N-Ar$, Ar is a substituted or unsubstituted aryl (e.g. phenyl, naphthyl, etc.), X is O or NH, and R is H or CH_3 . The following is a list of representative dye
 15 monomers useful in this invention:

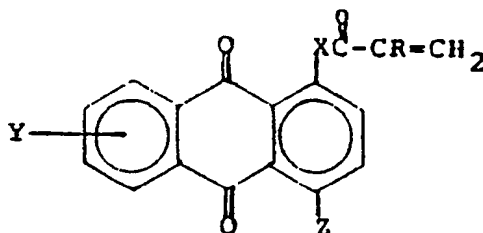




10 where R is N or CH₃, and R¹ is H or CN.

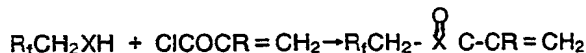


where X is O or NH, Ar is a substituted or unsubstituted aryl (e.g. phenyl, naphthyl, etc.), and R is H or CH₃.



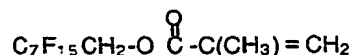
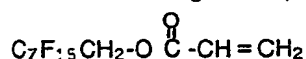
25 where Y and Z, which may be the same or different, are selected from -NO₂, -OR^{''}, -NHR^{''}, alkyl, aryl, and R^{''} is aryl or C₁ to C₈ alkyl, X is O or NH, and R is H or CH₃.

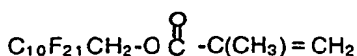
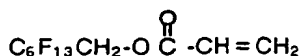
Non-dye monomer(s) used in chain-growth and step-growth polymers as well as the polymeric backbone of graft polymers can be partially-, or non-fluorinated, but preferably, non-dye monomer(s) are fluorinated and contain fluoroaliphatic groups. In step-growth polymers, the non-dye monomer(s) can be mono- or di-functional and the polymerizable groups can react with polymerizable groups on dye or other non-dye monomer(s) where mixtures of non-dye monomers are used to derive the polymer, to form linkages through step-growth polymerization reactions. Preferably said monomer(s) are di-functional, and their polymerizable groups are identical. In chain-growth polymers, the non-dye monomer(s) can have one or more ethylenically unsaturated groups, but preferably only one, which can react with ethylenically unsaturated groups on other non-dye or dye monomer(s) to form linkages between monomers through chain-growth polymerization reactions. If a monomer has more than one ethylenically unsaturated group, the groups need not be identical and the groups on other non-dye monomer(s) need not be identical. Non-dye monomers used to make the polymeric back bone in graft polymers are similar to those used in either step-growth or chain-growth polymers, but at least one of the monomer units comprising said backbone, must contain a reactive group, e.g. hydroxyl, carboxyl, haloformic, isocyanato, amino, acrylic, methacrylic, acrylamido, vinyl and allyl, that will react with the reactive group on the pendent-group-precursor compound(s) to form a linkage, and will not participate in the polymerization reaction used to make the polymeric backbone. Preferably, all polymerizable groups on non-dye monomer(s) will be terminal groups. A preferred class of non-dye monomers are fluorochemical acrylates which can be prepared by the condensation of suitable fluorochemical alcohols, amines or acrylamides with acrylic or methacrylic acid chlorides via the following reaction:



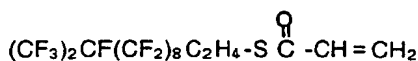
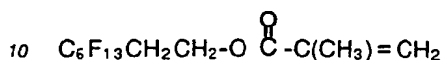
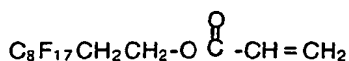
Where R_f is a fluoroaliphatic group, X is O or NH, and R is H or CH₃.

The following is a representative list of fluorochemical acrylates useful in this invention:

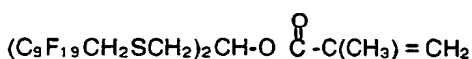
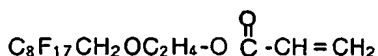




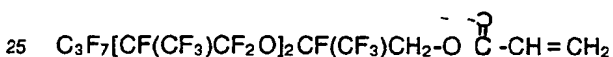
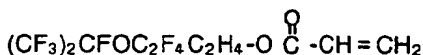
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Further description of the preparation of graft, step-growth and chain-growth polymers will be omitted in the interest of brevity since in most cases they follow classical methods such as described, for example, in W. R. Sorenson and T. W. Campbell, Preparative Methods of Polymer Chemistry 57-234 (1961), and H. A. J. Battaerd and G.W. Treyer, Graft Copolymers (1967).

30 The following specific but nonlimiting examples will serve to illustrate the present invention.

Example 1

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1-acryloxy-4-(p-tolylamino)anthraquinone, an acrylate dye monomer, was prepared by dissolving 2.0 g (0.0061 mole) of 1-hydroxy-4-(p-tolylamino)anthraquinone in 100 mL of chloroform. Said solution was heated to reflux and treated with 0.85 mL (0.61 g) of triethylamine. To this solution was added 0.49 mL (0.0061 mole) of acryloyl chloride dropwise over 15 minutes. The reaction was monitored by thin layer chromatog-

40 raphy. After 3 hours, some product had appeared, and the reaction mixture was treated with additional triethylamine and acryloyl chloride. After a total of 6 hours, thin layer chromatography showed some remaining starting material. The mixture was cooled, washed with water and dried over sodium sulfate. After solvent removal, a blue-violet solid remained which was purified by column chromatography, using silica gel and chloroform, to give the pure acrylate with a melting point of 164.5-166°C. The product was

45 recrystallized from hexane as fine, blue-violet needles which gave a red solution when dissolved in organic solvents like chloroform.

A copolymer of

$\text{C}_7\text{F}_{15}\text{CH}_2\text{-O}-\overset{\text{O}}{\parallel}\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$ (prepared by reacting methacryloyl chloride with 1,1-dihydroperfluorooctanol according to the method described in U.S. Pat. No. 2,642,416) and 1-acryloxy-4-(p-tolylamino)anthraquinone

50 was prepared by dissolving 10 g of the fluorochemical methacrylate, 0.862 g of the anthraquinone acrylate and 0.06 g of azobis(isobutyronitrile) (i.e. AIBN) in 60 g of 2,3,3-trichloroheptafluorobutane. The reactants were mixed in a 115 mL glass bottle then degassed by successive evacuations by an aspirator followed by flushing the bottle with nitrogen gas. After degassing, nitrogen gas was bubbled through the solution for 10

55 minutes. The bottle was then tightly sealed with a screw cap and placed in a Launder-O-Meter™ with the water bath set at 65°C. The reaction bottle was agitated in the water bath for 16 hours after which it was cooled and opened. The polymeric product, which formed a red solution, was filtered and the solvent was removed under reduced pressure. The solid, polymer product was soluble in "FREON 113".

"FLUORINERT" liquid, "FC-75", and was insoluble in and did not impart color to toluene or acetone which means that the product contained no free dye monomer, nor did it contain any homopolymer of the dye monomer since these would both be soluble in and would impart color to acetone or toluene.

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Examples 2-9

Examples 2-9 were prepared according to procedure of Example 1; however, different dye monomers, quantities of dye monomers, non-dye monomers, AIBN, "FREON 113", and in some cases, various quantities of a co-solvent, ethyl acetate were used. The dye monomer and quantities of each reactant used are summarized in Table 1.

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Table-1

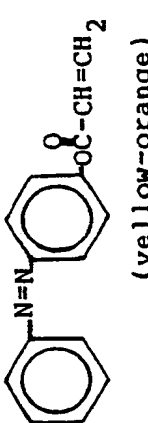
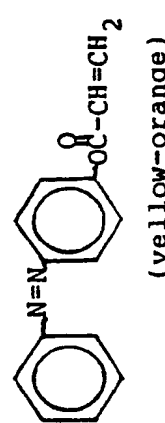
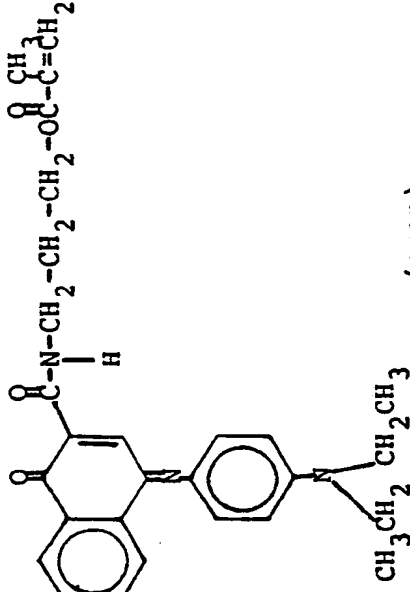
Example	Monomer structure (color)	Dye monomer (g)	Non-dye monomer (g)	AIBN "FREON 113" Ethyl acetate (g)
2	 (yellow-orange)	0.2	20	120
3	 (yellow-orange)	1.0	20	120
4	 (cyan)	0.0195	10	60

Table-1 Continued

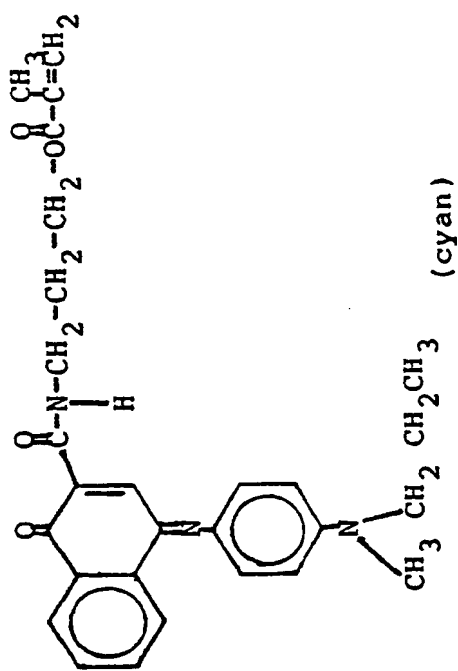
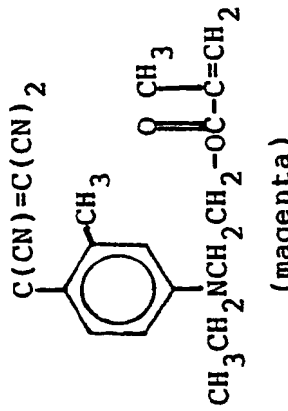
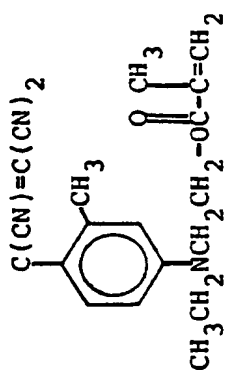
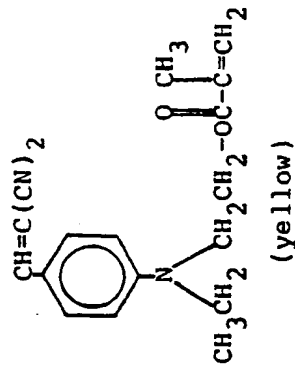
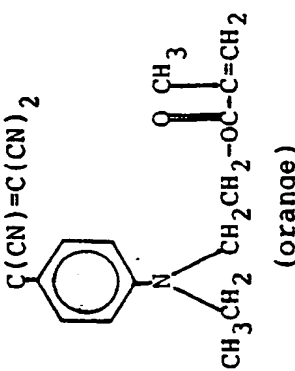
Example	Monomer structure (color)	Dye monomer (g)	Non-dye monomer (g)	AIBN (g)	"FREON 113" Ethyl acetate (g)
5	 (cyan)	0.058	10	0.06	2.1
6	 (magenta)	0.02	10	0.06	1.5

Table-1 Continued

Example (color)	Monomer structure	Dye monomer (g)	Non-dye monomer (g)	AIBN (g)	"FREON 113" Ethyl acetate (g)	
7	 (magenta)	0.0485	10	0.06	60	2.5
8	 (yellow)	0.0215	10	0.06	60	1
9	 (orange)	0.0215	10	0.06	60	1

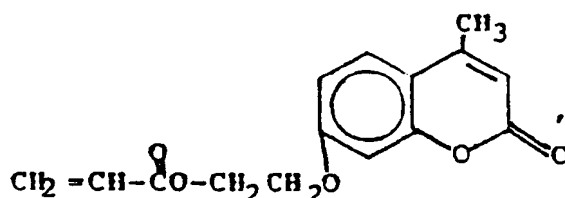
Example 10-12

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Examples 10-12 were prepared according to the procedure of Example 1; however, different, novel, dye monomers (the preparation of which are described below), and different quantities of dye monomer, non-dye monomer AIBN, and "FREON 113" were used, and in some cases, various quantities of a co-solvent, ethyl acetate, was used. The dye monomer, and the quantities of each reactant used are summarized in

5 Table 2.

The dye monomer used in Examples 10 and 11 was prepared by dissolving 3 g of 7-hydroxy-4-methylcoumarin in a solution of 0.60 g sodium hydroxide and 30 mL of water. A 1.37 g quantity of 2-chloroethanol was added to the solution and the mixture was refluxed for 5 hours. The crude product, which precipitated when the mixture was cooled to room temperature, was isolated by suction filtration and
 10 recrystallized from ethanol as white crystals, with a melting point of 144-146° C. A solution was prepared by dissolving 1.5 g of the white, crystalline product and 1.38 g of triethylamine in 30 mL of chloroform. This solution was refluxed while 1.23 g of acryloyl chloride was added dropwise. The solution was then stirred and refluxed for 3 hours and analysis by thin layer chromatography indicated complete reaction. The mixture was cooled to room temperature, and the solvent removed under vacuum. The crude product was
 15 recrystallized from ethanol to yield 1.27 g of the product,

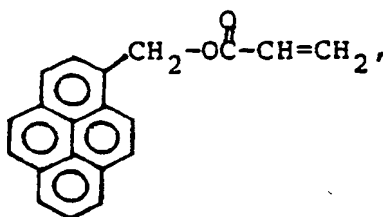


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which had a melting point of 90-92° C, and a proton NMR spectrum consistent with the assigned structure.

The dye monomer used in Example 12 was prepared by dissolving 1 g of 3-pyrenemethanal (prepared according to the procedure of Yoshimoto, et al., 46 Bulletin of the Chemistry Society of Japan 358, (1973)) in 60 mL of chloroform, and adding 0.88 g of triethylamine to the solution followed by 0.78 g of acryloyl chloride. The solution was then refluxed for 6 hours. After the solvent was removed, a yellow solid remained. The yellow solid was recrystallized from petroleum ether to yield 0.714 g of the white, crystalline, acrylate, product

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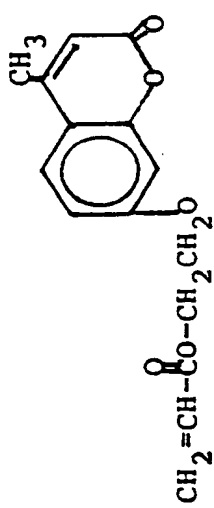
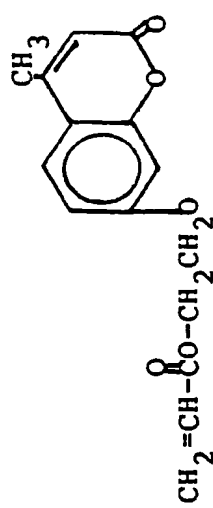
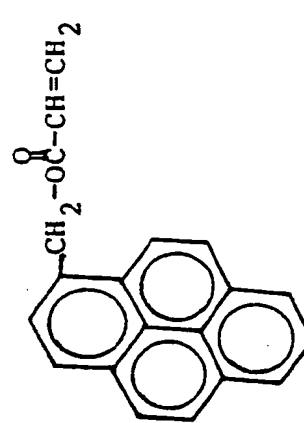
which had a melting point of 70-72° C and a proton NMR spectrum consistent with the assigned structure.

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Table-2

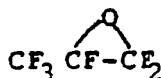
Example	Monomer structure (color)	Dye monomer (g)	Non-dye monomer (g)	AIBN (g)	Freon ^R 113 (g)	Ethyl acetate (g)
10		.125	10	.06	60	5
11		.257	10	.06	60	10
12		.1	10	.06	60	0

Example 13

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A fluorochemical, polycarbonate compound was prepared by a step-growth polymerization of a dye monomer and a bischloroformate monomer derived from a fluorochemical diol. The bischloroformate monomer, $\text{ClCOOCH}_2(\text{CF}_2)_3\text{OCF}(\text{CF}_3)\text{CH}_2\text{OCOCl}$, was prepared by reducing $\text{FCO}(\text{CF}_2)_3\text{OCF}(\text{CF}_3)\text{COF}$ (the 1:1 adduct of $\text{FCOCF}_2\text{CF}_2\text{COF}$ and

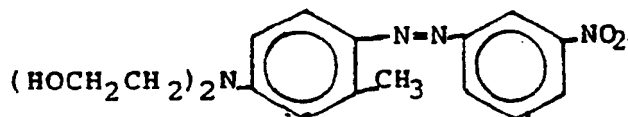
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made by the method described in U.S. Pat. No. 3,250,807 (Fritz)) with sodium borohydride, yielding $\text{HOCH}_2(\text{CF}_2)_3\text{OCF}(\text{CF}_3)\text{CH}_2\text{OH}$. Some of the diol was then reacted with phosgene to form the bischloroformate monomer. The dye monomer was

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Disperse Red 17 (color index No. 11210), available from Crompton and Knowles Corporation. 3.09 g of the bischloroformate monomer and 30 mL of tetrahydrofuran were placed in a reaction flask containing a magnetic stirring bar. A solution of 0.78 g of the dye monomer and 0.48 g of triethylamine was prepared in 15 mL of tetrahydrofuran and added dropwise to the stirred solution of the bischloroformate monomer. A fine solid of triethylamine hydrochloride formed during the addition. To this reaction mixture, an additional 0.78 g of the bischloroformate monomer and 0.48 g of triethylamine were added. After the addition, the reaction mixture was washed with water to remove the triethylamine hydrochloride salt by-product. The structure of the polycarbonate product, which formed a red solution in the tetrahydrofuran reaction solvent, was confirmed by IR and H-NMR spectral analysis. The polymer, isolated by removal of solvent, was a viscous red liquid soluble in acetone and benzotrifluoride and slightly soluble in "FREON 113". One drop of the above prepared polycarbonate dye was dissolved in 5 mL of a 30% by weight butyl acetate solution of a commercial fluorocarbon copolymer used as a conformal coating for electronic circuitry. The resulting polymer solution was coated on a clear plastic film using a #32 wire wound rod to give a solid, orange coating upon evaporation of the solvent.

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The names "FREON 113", "FLUORINERT", "FC-75", "FREON E", "FLUTEC PP", "GALDEN", and "Lauder-O-Meter" used above are trademarks.

40

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope of this invention.

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Claims

1. A fluorine-containing polymer characterized in that the polymer is colored, fluorescing or light absorbing and is selected from one of two classes, wherein the first class of polymers comprises

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interpolymerized, repeating units derived from:

(A) partially- or non-fluorinated, and non-chromophoric-moiety-containing monomer,

(B) partially- or non-fluorinated co-monomer which contains chromophoric moieties,

wherein at least one of said monomer or co-monomer contains a fluoroaliphatic radical; and

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the second class of polymers comprises a polymeric backbone of interpolymerized, repeating units derived from partially- or non-fluorinated, non-chromophoric-moiety-containing monomer said backbone having at least one pendent group grafted thereon said pendent group being derived from partially- or non-fluorinated, chromophoric-moiety-containing, pendent-group-precursor compound, wherein at least one of said monomer or pendent group contains a fluoroaliphatic radical.

2. The polymer of claim 1, further characterized by the feature that said first class polymers comprise 90 to 99.9 percent of said monomer (A) and 10 to 0.1 percent of said monomer (B) on the basis of total monomer weight, and said second class polymers comprise 90 to 99.9 percent polymeric backbone and 10 to 0.1 percent pendent group on the basis of total backbone and pendent group weight.

5 3. The polymer of any of the preceding claims, further characterized by the feature that said light absorbing polymer is a first class polymer and a chain-growth polymer.

4. The polymer of any of claims 1-3, further characterized by the feature that said light absorbing polymer is a chain-growth polymer, monomer (A) contains at least one polymerizable group selected from the group consisting of acrylic, methacrylic, acrylamido, vinyl and allyl groups, and co-monomer (B)
10 contains at least one polymerizable group selected from the group consisting of acrylic, methacrylic, acrylamido, vinyl and allyl groups.

5. The polymer of any of claims 1-2 further characterized by the feature that said light absorbing polymer is of the first class and is a step-growth polymer.

6. The polymer of any of claims 1-2 and 5, further characterized by the feature that said light absorbing
15 polymer is of the first class, is a step-growth polymer, monomer (A) contains at least one polymerizable group selected from the group consisting of hydroxyl, carboxyl, haloformic, isocyanato, and amino groups, and co-monomer (B) contains at least one polymerizable group selected from hydroxyl, carboxyl, haloformic, isocyanato and amino groups.

7. The polymer of any of claims 1-2, further characterized by the feature that said light absorbing
20 polymer is of the second class and is a graft polymer.

8. The polymer of any of claims 1-2, and 7, further characterized by the feature that said light absorbing polymer

is of the second class;

is a graft polymer;

25 has a polymeric backbone containing at least one reactive group selected from the group consisting of hydroxyl, carboxyl, haloformic, isocyanato, amino, acrylic, methacrylic, acrylamido, vinyl, and allyl groups; and

has at least one pendent group derived from a pendent-group-precursor compound containing at least one reactive group selected from the group consisting of hydroxyl, carboxyl, haloformic, isocyanato, amino,
30 acrylic, methacrylic, acrylamido, vinyl and allyl groups,

with the provision that said reactive group on the polymeric backbone will react with said reactive groups on the pendent-group-precursor compound, but neither the reactive group on the backbone nor the reactive group on the pendent-group-precursor compound will react with the polymerizable group on the monomer comprising the backbone.

35 9. A method of making the polymer of any of claims 1-6, further characterized in that it comprises reacting monomer (A) with monomer (B).

10. A method of making the polymer of any of claims 1,2,7 and 8, characterized in that it comprises polymerizing monomer to form a polymeric backbone, and reacting the polymeric backbone with the pendent-group-precursor compound.

40 11. A solution characterized in that it comprises the polymer of any of claims 1-8 and a fluorine-containing liquid.

12. A coating characterized in that it comprises the polymer of any of claims 1-8.

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Publication number: **0 323 060 A3**

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EUROPEAN PATENT APPLICATION

21 Application number: **88311678.2**

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88 Date of deferred publication of the search report:
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54 **Fluorine-and chromophore-containing polymer.**

57 Chromophoric-moiety-containing, polymeric materials, containing at least one fluoroaliphatic radical, which are useful as dyes or colorants for fluorine-containing liquids, as coatings or components of coatings which are colored, light-absorbing, or fluorescing and characteristic properties of fluorocarbon polymers, e.g. chemical inertness and hydrophobicity; and a method of detecting leaks in normally sealed devices, e.g. electronic devices, using a coating which includes the polymeric material, and a bath of a fluorine-containing liquid in which the coating is soluble.

EP 0 323 060 A3



European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 31 1678

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	EP-A-0 040 841 (DAIKIN KOGYO CO.) -----		C 08 F 246/00 C 09 D 3/74 C 08 F 299/00 C 08 F 8/00
D,A	US-A-4 619 990 (M.A. ELMASRY) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 F
The present search report has been drawn up for all claims			
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Analytical Studies on the Oxidative Degradation of the Reactive Textile Dye Uniblue A

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Oxidative degradation process of organic materials in wastewater is an area of significant current interest. In the case of commercial textile dyes, little is known about the structures of the actual products that can form once a dye has been submitted to oxidative conditions. Here, a product analysis approach was applied to identify some of the major early degradation products of Uniblue A (UBA) when reacted with peroxydisulfate (PDS). UBA is the vinyl sulfone form and major wastewater constituent of the commercial anthraquinone textile dye C.I. Reactive Blue 19. Using NMR, LC-MS, and Raman, four reaction products could be identified, and possible reaction pathways are discussed.

Introduction

Purpose and Scope of the Work. Wastewater management is a major concern for many industries but in particular for the textile dyeing industry (1). Here, reactive dyes pose a particular problem because, among other reasons, they are relatively expensive, tend to hydrolyze in the dyeing bath, and up to 60% of the applied reactive dye can end up in the wastewater (2). Commonly, oxidative processes are used for treatment of such effluents. Often, this involves the use of reactive oxygen species, which can generate free radicals at the structural backbone of the dyes. For most dyes, little is known about the actual reaction pathways that occur after the initial attack. Similarly, dye degradation product analysis has seldom been reported when using industrially important textile dyes, even though product analysis can lead to considerable mechanistic understanding. Undoubtedly, this insight could be useful in the effective control of undesired reactions in industrial dye degradation processes. In this context, we describe here the detailed analysis of some of the major, early degradation products of Uniblue A (UBA) from its reaction with peroxydisulfate (PDS) and discuss possible reaction pathways.

Uniblue A (UBA). This dye is the vinyl sulfone form of the anthraquinone dye C.I. Reactive Blue 19, which is used industrially to dye cellulosic substrates including cotton fabrics and which is one of the highest volume reactive dyes on the market. UBA has been reported to be the predominant constituent of textile wastewaters where C.I. Reactive Blue 19 is used in the dyeing process (3, 4). Hence, it is of immediate

environmental interest to study its oxidative degradation chemistry. UBA has considerable structural complexity on one hand (amino and sulfone groups, quinoid structure), while the absence of tautomerism (as in the case of α -hydroxyazo dyes) renders it feasible for detailed product analysis and meaningful mechanistic interpretations. Much of the published chemistry of C.I. Reactive Blue 19 has concerned the vinyl sulfone reactive moiety of the dye and is well-documented in the literature (5-8). On a different note, the formation of UBA aggregates in aqueous solution has been reported (9) but under neutral to alkaline conditions only. Hence for mechanistic reasons, dye degradation studies are best carried out under moderately acidic conditions because of its higher solubility through possible protonation of the amino groups.

Peroxydisulfate (PDS). This strong oxidant ($E = +2.05$ V) has long been used industrially for the destruction of hydraulic fluids in the petroleum industry as an industrial bleach and reaction initiator. Recently, it was suggested to be a useful reagent for the destruction of organics in hazardous wastewaters through a process named Direct Chemical Oxidation (DCO), where the oxidant could be regenerated by electrolytic methods (10, 11). Even though PDS can also undergo ionic reactions (12, 13), its main application of interest is the thermal or photochemical generation of the sulfate radical anion $\text{SO}_4^{\cdot-}$ through homolysis of the peroxide bond. At $\text{pH} > 3$, this is the only reaction, while at $\text{pH} < 3$, $\text{HS}_2\text{O}_8^{\cdot-}$ is formed, which decays to give sulfur tetroxide and bisulfate (14). At $\text{pH} > 8.5$, $\text{SO}_4^{\cdot-}$ is known to produce HO^{\cdot} upon reaction with HO_2^{\cdot} (15). Therefore, unequivocal mechanistic studies with $\text{SO}_4^{\cdot-}$ are best carried out between $\text{pH} 3$ and $\text{pH} 8.5$. In recent work by Salem et al. (16), the oxidation of coumarin-1, a laser dye, by PDS was reported. A nonradical reaction mechanism where the dye acts as a nucleophile and PDS is the electrophile was proposed, based on the evidence that the radical trap allyl acetate did not affect the dye fading kinetics.

Experimental Section

Materials. All chemicals, unless otherwise noted, were purchased from Aldrich and used as received. Uniblue A was 90% pure and purified with a semipreparative column as described below. Potassium peroxydisulfate was purchased from Fluka. Quinizarin-2-sulfonic acid was purchased from the Sigma Library of Rare Chemicals. The water used in all experiments was distilled and passed through a Milli-Q deionization system.

Chromatography. HPLC measurements were performed on a Waters LC module 1, using a Waters 996 PDA detector. A Nucleosil C18 (250×4.6 mm) 100 \AA $5 \mu\text{m}$ column was used for all analytical separations while the corresponding corresponding semipreparative column, C18 Nucleosil (250×10 mm) 100 \AA $5 \mu\text{m}$, was used for large-scale separations. A mobile phase consisting of 70:30, methanol:10 mM phosphate buffer, $\text{pH} 6.7$, was utilized at a flow rate of 0.5 mL/min for analytical separation. The same mobile phase was used with the semi-prep LC at a flow rate of 2.3 mL/min for the preparative separation of isolated fractions. A 103-mL sample of a 4 mM Uniblue A solution (initial reaction concentration) was injected using a 5-mL injection loop. Isolated fractions were collected and stored under nitrogen at 0°C . Relative product percentages of total dye decomposition products are based on amount of material collected and the degree of dye decomposition under standard reaction conditions. The further separation of peaks 3 and 4 (see Figure 1) was accomplished at a flow rate of 0.7 mL/min (on the analytical

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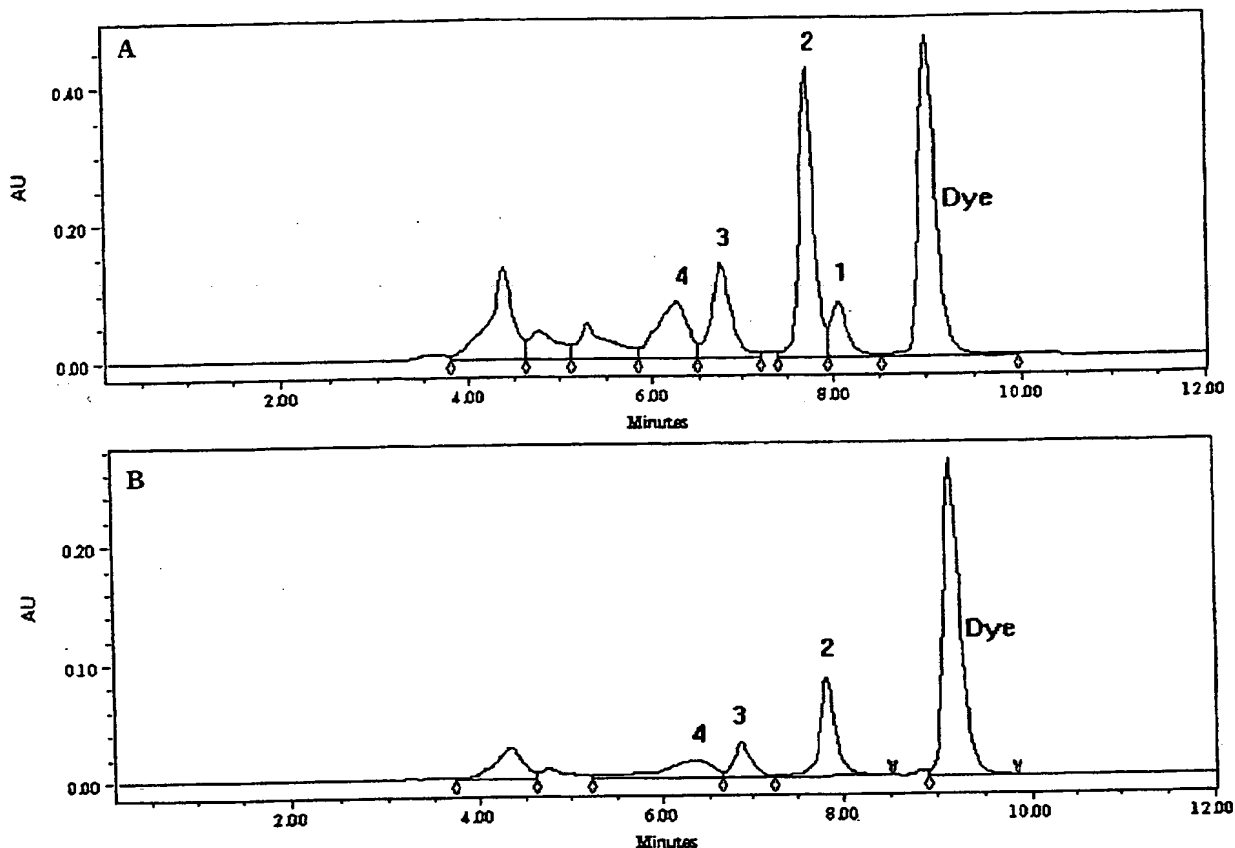


FIGURE 1. Chromatograms of UBA reactions with PDS ($\lambda = 254$ nm). The numbers 1–4 correspond to the products shown in Figure 2. (A) 1 mM UBA + 2 mM peroxydisulfate at 65 °C for 7 h. (B) 0.1 mM UBA + 0.2 mM peroxydisulfate at 65 °C for 7 h.

column; 3.3 mL/min on the preparative column) with a mobile phase of 50:50, methanol:10 mM phosphate buffer, pH 6.7.

NMR. One-dimensional proton NMR data and two-dimensional homonuclear and heteronuclear chemical shift correlation NMR data were collected on a Bruker DMX-500 spectrometer using a 5-mm ^1H triple axes inverse (TXI) probe with triple axes gradients. Proton resonances were used for the identification of decomposition products of UBA. To obtain more detailed structural information, the proton chemical shifts were correlated to the ^1H chemical shifts using homonuclear correlation spectroscopy (COSY) and correlated to the ^{13}C chemical shifts using heteronuclear multiple quantum coherence spectroscopy (HMQC) and heteronuclear multiple bond correlation spectroscopy (HMBC). NMR samples were run on the total mass of each of the products collected in dimethyl sulfoxide- d_6 (DMSO). Carbon-13 NMR data were collected at 100.6 MHz on a Bruker DMX-400 spectrometer using 5 mm ^{13}C broad band observe probe. Distortionless enhancement by polarization transfer (DEPT-135) experiment was acquired at 125.8 MHz on a Bruker DMX-500 spectrometer using a broad band observation probe for distinguishing CH_2 and CH groups. The 1D and 2D NMR data sets were processed with the Bruker XWINNMR software, operating on UNIX workstations. All NMR experiments were performed at 300 K. DMSO was used as a solvent for all NMR experiments.

^1H . The spectrum was measured in a 5-mm NMR tube with 90° ^1H pulse for 7.5 μs . One thousand transients were accumulated with a 3-s relaxation delay between pulses. Total experiment time: 1 h. Spectral width: 2500 Hz. COSY: F2

(proton) time domain, 2000 data points, spectral width 2500 Hz, 32 scans; F1 (proton) time domain, 256 rows. HMQC: F2 (proton) time domain, 2000 data points, spectral width 2500 Hz, number of scans 128 and 256; F1 (carbon-13) time domain, 256 rows, spectral width 7500 Hz. HMBC: F2 (proton) time domain, 2000 data points, spectral width 2500 Hz, number of scans 128 and 256; F1 (carbon-13) time domain, 256 rows, spectral width 14 kHz.

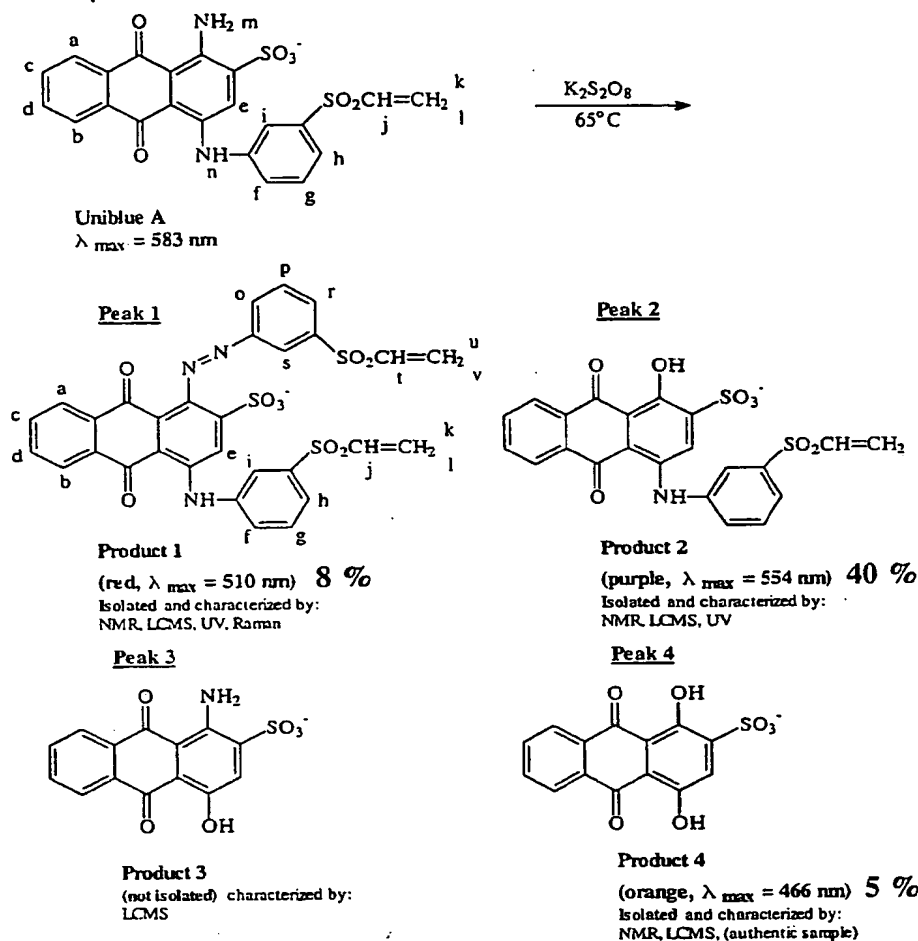
^{13}C . The spectrum was measured in a 5-mm NMR tube with 90° ^{13}C pulse for a 9.5 μs . Ten thousand transients were accumulated with a 5-s relaxation delay between pulses. Spectral width: 22 kHz.

DEPT-135. The spectrum was measured in a 5-mm NMR tube with ^1H decoupler pulses of 90° pulse for 5.5 μs , 180° pulse for 11 μs , and 135° pulse for 10 μs . Five thousand transients were accumulated with a 10-s relaxation delay between pulses. Spectral width: 27 kHz.

MS/LC-MS. These experiments were conducted on a Finnigan MAT LCQ Ion Trap mass spectrometer using negative ion electrospray in the full-scan mode. Typical source operating conditions were 3.5 kV spray voltage, heated capillary temperature of 200 °C, and sheath and auxiliary gas flows of 60 and 20 au, respectively. The UBA reaction mixtures were separated with a Nucleosil C18 100/5 μm 150 \times 2.1 mm column using 65/35, methanol:10 mM ammonium acetate, as the mobile phase flowing at 0.2 mL/min. All fraction collected peaks (from semi-prep) were analyzed by direct infusion. Tandem MS experiments were conducted by direct infusion into the mass spectrometer.

IR/Raman. *Infrared.* The spectrum was acquired on a Bio-Rad FTS-40 spectrometer with a DTGS detector. The dye

SCHEME 1. Major Decomposition Products Resulting from the Degradation of UBA (4 mM) with PDS (8 mM) at 65 °C



was mixed and ground with KBr in ca. 1/10 ratio and analyzed by diffuse reflectance (DRIFTS). Thirty-two scans were coadded and averaged at a resolution of 8 cm^{-1} .

Raman. The same dye/KBr mixture described above was pressed into a pellet. The Nicolet Raman 950 FT-Raman spectrometer was used. A near-IR laser (1064 nm) excited the Raman scattering. A power of 0.26 W was incident on the sample. A total of 1024 scans was coadded and averaged. The scattering was detected with a liquid nitrogen-cooled Ge detector.

Standard Reaction Conditions and Impact on Products Identified. Degradation reactions of UBA (0.1 and 1 mM) were carried out with PDS (0.2 and 2 mM $\text{K}_2\text{S}_2\text{O}_8$, respectively) at 65 °C for 7 h and left open to air, unless otherwise mentioned. The initial pH of the solutions was approximately 5.5 and decreased gradually over time to pH 3 for the 1 mM UBA reactions and to pH 5.2 for the 0.1 mM UBA reactions. No buffer was used to facilitate MS analysis. Additionally, control reactions were run at constant pH values of 5.5 and 3.0 (preadjusted with H_2SO_4 and kept constant during the reaction by stepwise addition of diluted NaOH solution). Also, for the purpose of product isolation only, the experiments were repeated at higher concentrations of UBA (2 and 4 mM) and PDS (4 and 8 mM, respectively). In all cases the same major decomposition products could be identified by LC and LC-MS, except for the run at 0.1 mM UBA (0.2 mM PDS) concentration, where no peak for 1 could be detected.

Radical Scavenging Experiments. A sample of 1 mM allyl alcohol was used in the standard dye reaction of 1 mM UBA and 2 mM $\text{K}_2\text{S}_2\text{O}_8$ at 65 °C.

Product Identification

Four products could be separated and identified from the reaction of UBA and PDS. Typical LCs are shown in Figure 1. The structural assignments are summarized in Scheme 1 and are discussed below.

Uniblue A. To structurally identify the dye decomposition products, it was first necessary to understand the NMR characteristics of the dye itself. Its structure is shown in Scheme 1 (including labels); the ^1H NMR and the COSY (homonuclear correlation spectroscopy) are depicted in Figure S1 (see Supporting Information). The protons that belong to the same spin system were sorted out by COSY. The assignments including ^{13}C and HMBC (heteronuclear multiple bond correlation spectroscopy) are displayed in Table 1 (spectra not shown). The short- and long-range molecular connectivity were used to map out the entire molecular structure.

Product 1. The material corresponding to peak 1 was identified as 1, as shown in Scheme 1. Typically, 12.4 mg (0.018 mmol) of this product was collected from prep-LC runs and represents roughly 8% of the total dye decomposition products from the standard degradation reaction at an initial dye concentration of 4 mM. With respect to UBA, ^1H

TABLE 1. Assignments of NMR Resonances of Uniblue A

¹ H ^a	δ ^b	δ ^c	COSY	HMBC
a, b	8.28 (q, J ₁ 13.75 Hz, J ₂ 7.47 Hz)	126.9	H _c , H _d	H _a , C _c , H _b , C _d
e	8.04 (s)	123.6		
c, d	7.89 (m)	133.8, 134.5	H _a , H _b	H _c , C _a , H _d , C _b
i	7.73 (s)	121.0		H _i , C _g , C _h
g	7.69 (t, J 7.78 Hz)	131.9	H _f , H _h	H _g , C _i , C _h
h	7.62 (d, J 7.98 Hz)	127.5	H _g	H _h , C _g , C _i
f	7.59 (d, J 7.75 Hz)	122.6	H _h	H _f , C _h
j	7.16 (q, J ₁ 16.45 Hz, J ₂ 9.85 Hz)	139.1	H _k , H _i	H _j , C _k , C _i
k	6.40 (d, J ₁ 16.44 Hz)	130.2	H _j	H _k , C _j
l	6.25 (d, J ₁ 9.83 Hz)	130.2	H _j	H _i , C _j

^a Letters refer to aromatic and vinyl protons. Blanks are due to singlet or unobserved correlation. ^b Proton chemical shift values (δ) are followed by the apparent splitting patterns (s, d, t, or q) and apparent coupling constants (Hz). ^c Carbon-13 chemical shift values (δ) obtained from HMQC.

TABLE 2. Assignments of NMR Resonances of Product 1

¹ H ^a	δ ^b	δ ^c	COSY	HMBC
s	8.23 (s)	120.73		H _s , C _r
a	8.22 (d) ^d	126.40	H _a , H _c	H _a , C _b , C _d
r	8.16 (d, J 7.94 Hz)	128.14	H _r , H _p	H _r , C _o
e	8.12 (s)	119.07		
p	8.10 (d, J 7.93 Hz)	129.32		
b	7.98 (d) ^d	126.48		H _b , C _a
d	7.94 (t) ^e	130.76		H _d , C _a
c	7.93 (t) ^e	130.76	H _c , H _b	H _c , C _d
i	7.88 (s)	121.43	H _i , H _f	H _i , C _g
g	7.86 (t) ^e	134.17	H _g , H _i	H _g , C _i
o	7.77 (t) ^e	128.03		H _o , C _r
h	7.75 (d) ^d	131.11		H _h , C _r
f	7.70 (d) ^d	131.08		H _f , C _h
l	6.25 (d, J 9.92 Hz)	129.26	H _i , H _j	H _i , C _k
k	6.39 (d, J 16.33 Hz)	129.26	H _k , H _j	H _k , C _i
u	6.31 (d, J 9.92 Hz)	130.72	H _u , H _t	H _u , C _t
v	6.46 (d, J 16.48 Hz)	130.72	H _v , H _t	H _v , C _t
j	7.15 (q, J 19.77, J ₂ 16.48 Hz)	136.51	H _j , H _{l,k}	H _j , C _{l,k}
t	7.24 (q, J 19.76, J ₂ 16.48 Hz)	136.53	H _t , H _{u,v}	H _t , C _{u,v}

^a Letters refer to aromatic and vinyl protons. Blanks are due to singlet or unobserved correlation. ^b Proton chemical shift values (δ) are followed by the apparent splitting patterns (s, d, t, or q) and apparent coupling constants (Hz). ^c Carbon-13 chemical shift values (δ) obtained from HMQC. ^d Unresolved doublets. ^e Unresolved triplets.

NMR indicates the presence of an additional vinyl sulfone group and approximately four aromatic protons, as seen in Figure S2 (see Supporting Information). Table 2 summarizes the data obtained on this reaction product. Figure S3 (see Supporting Information) shows the HMBC spectrum of the aromatic region. HMBC represents the connectivity between the nonprotonated carbonyl resonances of the quinone ring and the protons H_a and H_b. Also the assignments of the protons H_d and H_e were derived from their corresponding carbons, which showed that the unfunctionalized part of the anthraquinone moiety remained intact. The proposed structure of 1 is further supported by a ¹³C and a DEPT-135 NMR experiment (spectra not shown). Most importantly, mass spectrometry experiments give an ion *m/z* 662 for peak 1. This mass accounts for an addition of 179 mass units, corresponding to the anilino vinyl sulfone side chain addition to a radical of the dye itself. Figure S4 (see Supporting Information) depicts the fragmentation pattern of *m/z* 662 constructed from tandem MS data. The fragmentations are consistent with that of the dye (loss of 64 and 91) (Figure 2). The loss of 28 is indicative of N₂. This is substantiated by the fact that the change from *m/z* 662 to *m/z* 634 is a neutral loss and an odd number of nitrogens is present. Raman spec-

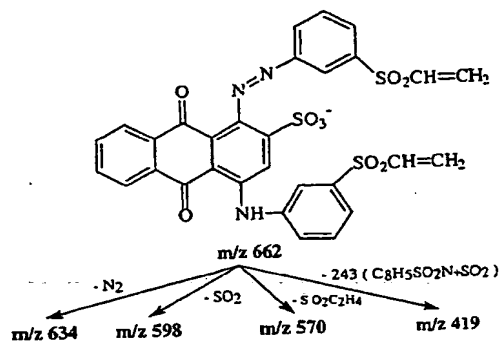


FIGURE 2. Fragmentation pattern of 1.

troscopy indicate the presence of the azo linkage, with a peak at 1460 cm⁻¹, where there was no detection of a peak in the IR (Figure S5, see Supporting Information). It has been reported that the azo linkage in azobenzene has been detected at 1510 cm⁻¹ for the cis isomer and from 1460 to 1380 for the trans isomer (17–19), which is therefore the most likely structure in our case as well.

Product 2. The material corresponding to peak 2 was identified as 2, as shown in Scheme 1. Under standard reaction conditions at an initial dye concentration of 4 mM, 48.8 mg (0.096 mmol) of 2 was collected, representing roughly 40% of the decomposition products. Product 2 was formed by the oxidation of the primary aromatic amino group on the anthraquinone ring. NMR data (not shown) are nearly identical to those of the dye. Mass spectrometry data (Figure S6, see Supporting Information) further support the assigned structure by showing a [M – H] one mass unit higher than that of the dye (*m/z* 484 vs *m/z* 483). The change in mass to an even number indicates that there is an odd number of nitrogens on the molecule (original dye contains two nitrogens). The MSMS experiments afforded the same fragmentation pattern as UBA itself (not shown).

Product 3. Peak 3 of the LC chromatogram is of a vinyl-hydrolyzed form of 2 and 1-amino-4-hydroxyanthraquinone-2-sulfonic acid 3, as identified by LC–MS (*m/z* 318, not shown). Other minor components are also found in peak 3, but they remain to be identified.

Product 4. The main component of peak 4 has been identified to be quinizarin-2-sulfonic acid (1,4-dihydroxyanthraquinone-2-sulfonic acid), as shown in Scheme 1. Figure 3 shows a comparison of the UV–vis of 4 and commercial quinizarin-2-sulfonic acid and the LC separation of the two products. These products exhibited the exact same retention time, and a co-injection resulted in only one single peak. MS and NMR experiments of the isolated fraction and commercial source have further confirmed the identity of 4 to be quinizarin-2-sulfonic acid (spectra not shown). The approximately 4 mg of quinizarin-2-sulfonic acid collected was found to represent approximately 5% of the total dye decomposition products.

Mechanistic Studies

Oxygen? The UBA and PDS reaction was carried out both open to air and under an inert atmosphere and a degassed reaction solution. The then-obtained LCs are in both cases identical to those in Figure 1. Apparently, oxygen does not play a role in the formation of the identified reaction products.

Radical or Nonradical? For comparative purposes, PDS self-decomposition was followed in the presence of 1 mM NaCl to probe the effect of ionic strength. From Figure 4, it is apparent that ionic strength does not play a major role in the PDS decomposition. Additionally, it is evident that PDS decomposes at a faster rate when in the presence of UBA.

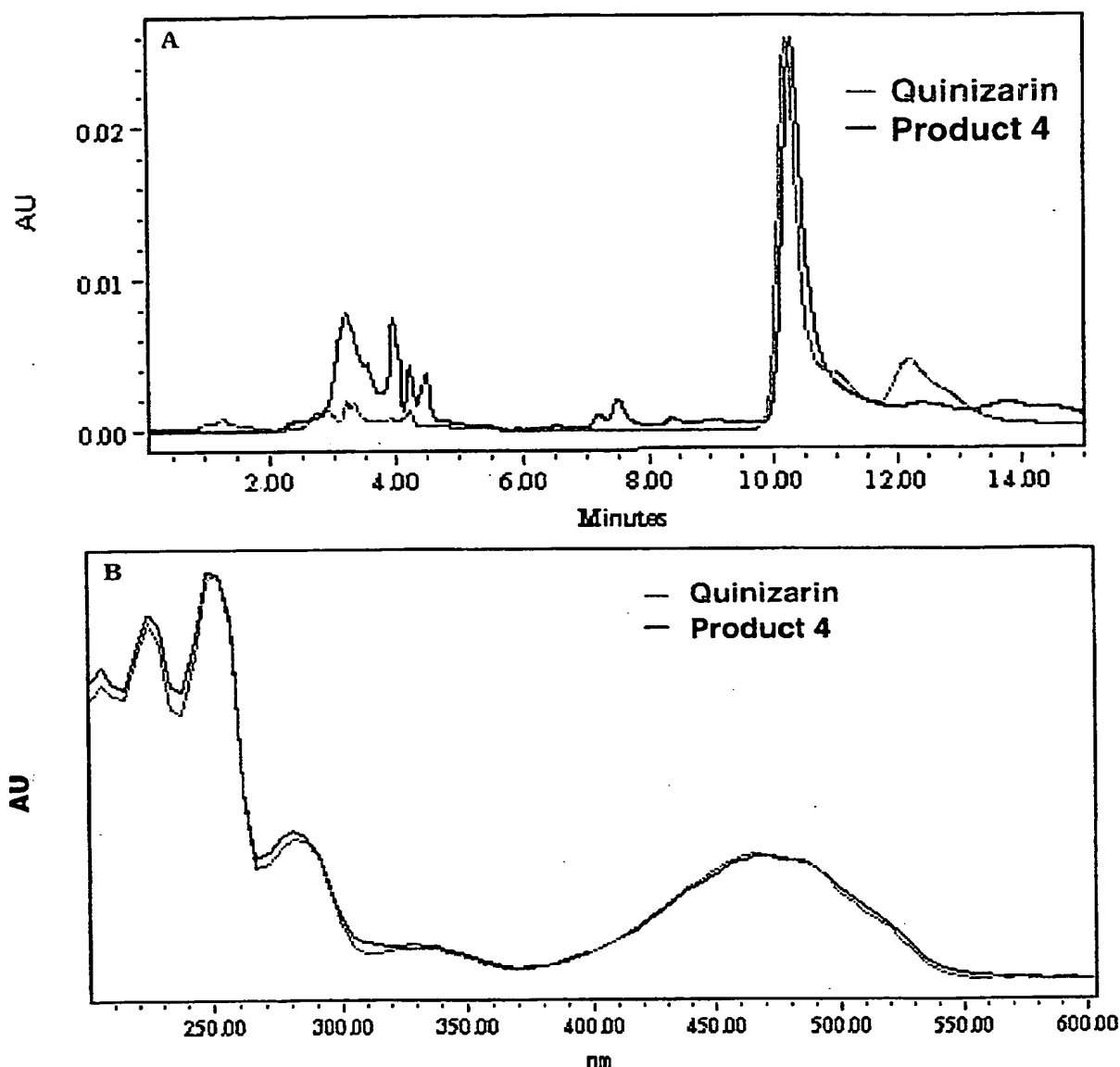


FIGURE 3. Comparison of LC behavior and absorbance of 4 with quinizarin. (A) LC separation of 4 and quinizarin. (B) UV spectra of 4 and quinizarin.

indicating that the dye does not react solely with free $\text{SO}_4^{\cdot-}$ but with PDS directly ($\text{S}_2\text{O}_8^{2-} + \text{UBA} \rightarrow \text{products}$) or with a caged $\text{SO}_4^{\cdot-}$, which may be in equilibrium with PDS itself ($\text{S}_2\text{O}_8^{2-} \rightleftharpoons 2\text{SO}_4^{\cdot-} \rightarrow \text{products}$). To know whether the mechanism involves radicals or not, a sulfate radical scavenger was added to the reaction mixture to see if a decrease in dye decomposition could be detected. With the addition of 1 mM allyl alcohol, which has been reported to react with $\text{SO}_4^{\cdot-}$ with a rate constant of $7.4 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$ (20), dye degradation was completely inhibited. Hence, the second possibility is the most likely one. After approximately 4 h, the rate of UBA consumption decreases while the decomposition of PDS continues. This indicates that PDS is oxidizing UBA decomposition products forming secondary oxidation products.

Volatiles? Additionally, the possibility of almost total degradation of the dye into volatiles such as benzene, for one, was explored. Analysis of the headspace of a sealed

reaction of UBA and PDS was performed. Nothing was detected by GC, while a blank experiment with benzene (2 mM in solution, 10 mL of headspace volume injected) added to the reaction mixture gave a clear signal.

Proposed Reaction Pathways. Figure 5 contains three possible UBA dye fading pathways leading to the formation of the major product 2. As indicated above, we believe PDS acts in a radical process through $\text{SO}_4^{\cdot-}$. The latter species is generally accepted to react primarily as an one electron oxidant (21), especially with aromatic compounds (22–24), and only in a few instances have hydrogen abstraction (25) or addition reactions (23) been observed. In contrast, the less selective hydroxyl radical has been shown to react more or less randomly by multiple mechanisms through all three types of mechanism, and the formation of major amounts (poly)hydroxylated aromatic products is very characteristic for the latter species (26). In our study with PDS and UBA, the formation of 2 is best explained by proposing the radical

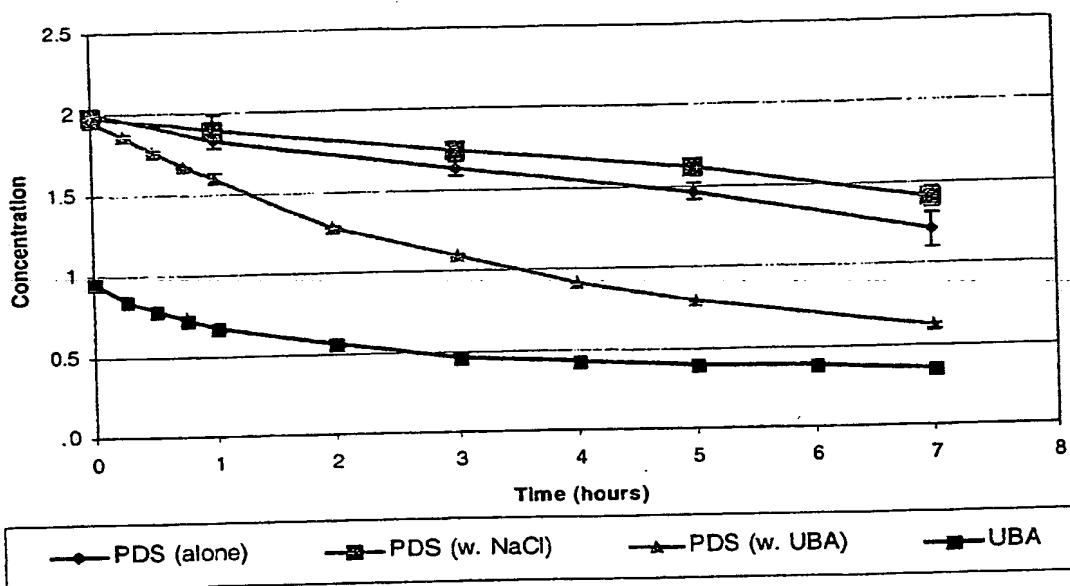


FIGURE 4. Decomposition study of PDS and UBA.

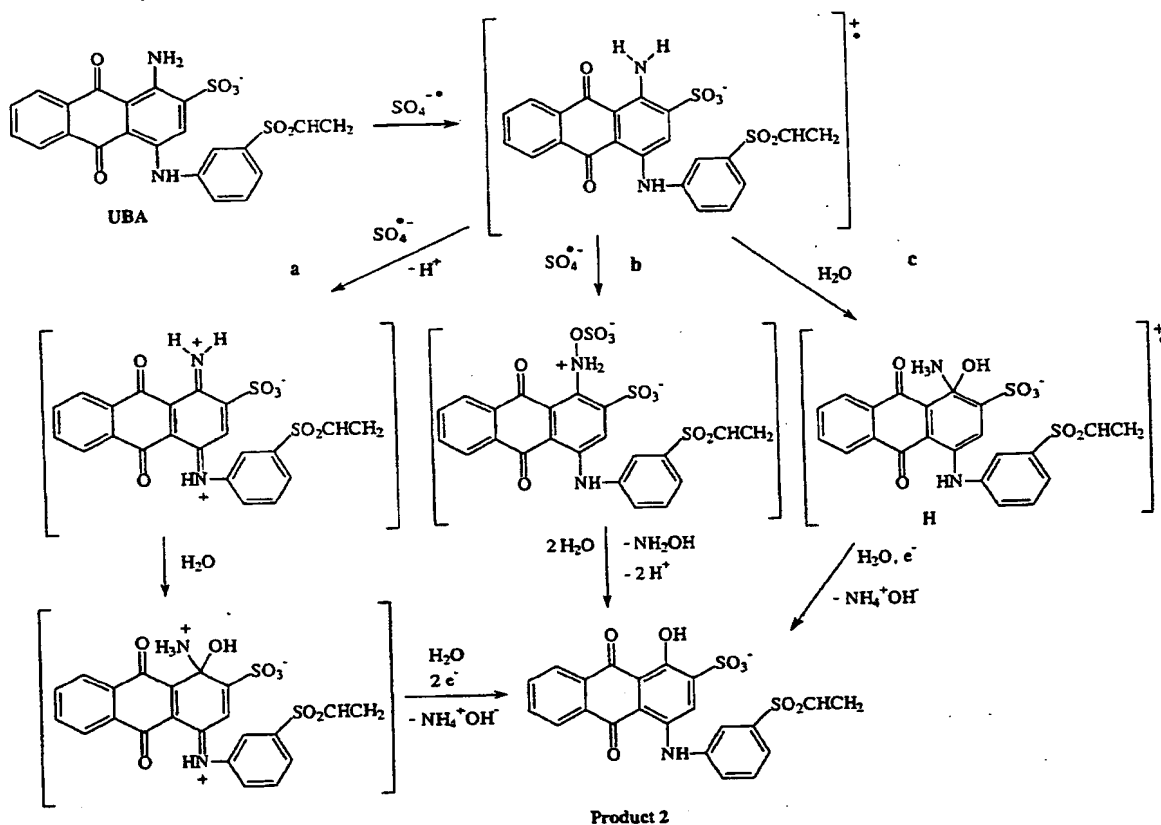
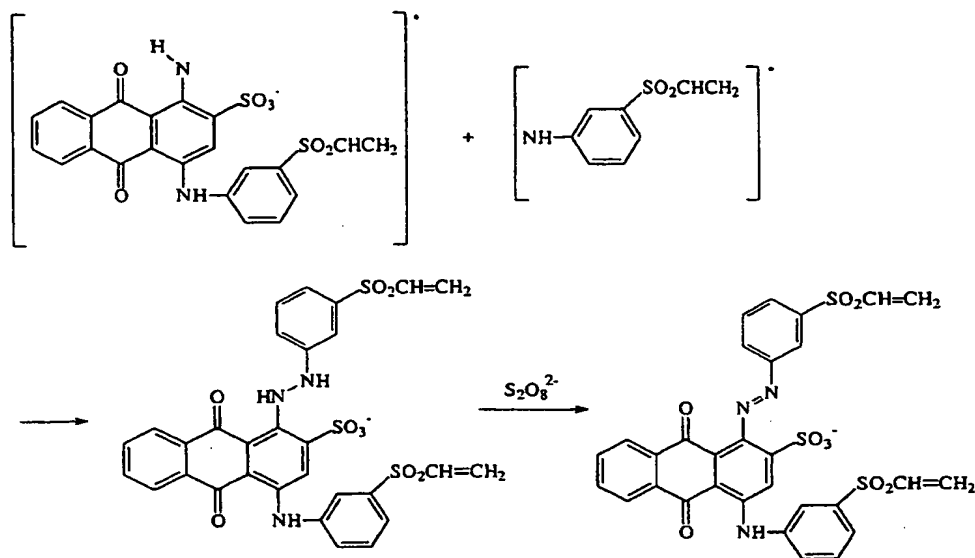


FIGURE 5. Possible reaction pathways for the decomposition of UBA with PDS yielding the major product 2.

cation of the dye as the first intermediate. In fact, when UBA is treated with one-electron oxidizing reagents, convincing evidence for the formation of a UBA radical cation has been reported already (27–29). Subsequently, there are three possible pathways leading to 2: (a) further oxidation to a bis-cationic quinoid structure followed by aromatic substitution, where subsequently two reducing equivalents could

come from other dye molecules; (b) adduct formation of the dye radical cation with $\text{SO}_4^{\bullet-}$ followed by double hydrolysis; or (c) direct aromatic substitution followed by one-electron reduction and hydrolysis. Even when using simple model compounds such as aromatic amines (30), no pathway can unequivocally be confirmed or ruled out, and some speculation remains unavoidable at this time. Also the formation of

SCHEME 2. Proposed Pathway for Formation of Reaction Product 1



3 and 4 can easily be rationalized in a similar way. Product 3 might arise from reaction of UBA at the vinylsulfonylphenyl-substituted nitrogen. Product 4 may arise from further oxidation of 2 or 3. Thus, for the formation of 2–4, the sulfate radical anion most likely reacts through one-electron oxidation of the dye. To the best of our knowledge, there is no reasonable way to explain the formation of these products through a hydrogen abstraction or aromatic addition process.

Clearly, at UBA concentrations of 1 mM and higher, however, the pathway for formation of 1 provides a distinctive, different look into the dye degradation process. Here we believe that either direct hydrogen abstraction at the $-NH_2$ group by PDS or radical cation formation of UBA with subsequent aminyl proton loss take place. The former mechanism was suggested by the work of Gupta and Srivastava using simple aromatic amines (31). Under acidic conditions, similar to our study, they reported azo bond formation from the oxidation of 4-chloro-2-methylaniline by PDS through hydrogen abstraction at the $-NH_2$ groups and subsequent coupling of the so-formed anilinoradicals to yield the corresponding hydrazine species, which was then further oxidized by PDS to give the azo compound. Using various aromatic amines, many results have been obtained that led to similar mechanistic conclusions (32–36). On the basis of this general reaction scheme, we propose in Scheme 2 a comparable pathway for the formation of 1. The anilino vinyl sulfone radical could be formed from the further degradation of 2, where the anilino vinyl sulfone part is liberated in the process of the formation of 4. Here, the free anilino vinyl sulfone could then again react with the sulfate radical anion through hydrogen abstraction or radical cation formation followed by proton loss, both of which would yield the anilino vinyl sulfone radical species required for the formation of 1. Similarly, the anilino vinyl sulfone radical could be formed during the formation of 3 from UBA itself.

Finally, for those cases where UBA concentrations of 1 mM as well as 2 and 4 mM were used, the last two of which were run for product collection purposes only, possible heterogeneous effects cannot be entirely ruled out (9), but our chosen acidic reaction conditions render this possibility unlikely (31).

In summary, the detailed analysis of some of the major early dye decomposition products derived from the oxidative degradation of UBA has provided valuable insights into the

reaction mechanism of potassium peroxydisulfate with anthraquinone dyes. Three possible reaction pathways, all occurring at the 1,4-diamino moiety of UBA and based on initial one-electron oxidation of the dye, are proposed to explain the formation of 2–4, while 1 arises most likely through radical coupling mechanism and subsequent oxidation of the so-formed hydrazine to the corresponding azo species. Because peroxydisulfate is currently being used in an emerging, alternative oxidation technology called direct chemical oxidation (DCO) (37) and because UBA is an important commercial dye, it would be interesting to degrade UBA under DCO conditions. Especially the possibility of the formation of a product like 1, which contains an electron-withdrawing and hence oxidation potential-increasing azo group might represent a challenge to any oxidative technique. For example, in oxidative activated sludge processes, only 3 out of 18 azo dyes were biodegraded (38).

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Supporting Information Available

Figures S1–S6 showing the NMR spectrum of UBA; the NMR, MS, Raman, and IR spectra of 1, and the MS spectrum of 2 (6 pages). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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